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Synthesis and Characterization of Cerium Tetraphenylporphyrin Nitrate and Molecular Recognition for NO

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Cerium (III) tetraphenylporphyrin nitrate Ce(TPP)NO₃ was synthesized by using meso-tetraphenylporphyrin (TPP) and Ce(NO₃)₃·6H₂O in mixture solution of CHCl₃ and C₂H₅OH (V:V=1:1). The complex was characterized by UV-Vis, FT-IR, conventional fluorescence, MALDI-TOF-MS, and ¹H NMR spectral techniques. The structure of complex was proposed via Spectral analyses, in which tetraphenylporphyrin was coordinated to a cerium ion in a tetradentate fashion, while one nitrate was coordinated to the same cerium ion. After bubbling NO to the solution of Ce(TPP)NO₃ in CH₂Cl₂, spectral analyses suggested that Ce(TPP)NO₃ could interact with NO to form a novel complex of Ce(TPP)(NO)NO₃, and NO was coordinated to the center cerium ion. When nitrogen was poured into the Ce(TPP)(NO)(NO₃) solution, the complex could be reduced to Ce(TPP)NO₃.

Key words: Cerium (III) tetraphenylporphyrin nitrate, NO, Molecular recognition

I. INTRODUCTION

The importance and versatility of porphyrin macrocycle and its metal-complexes in nature has inspired considerable efforts to understand, mimic, and expand the role of metalloporphyrins through the use of model systems [1]. Metal porphyrin compounds used as catalyst, indicator, and new functional material have attracted researchers' interests [2–4]. Cerium and other lanthanide porphyrin derivatives have been synthesized and investigated for more than three decades regarding their functional properties and potential for molecular architecture [5, 6]. However, the complex of Ce(TPP)NO₃ has not been reported so far.

Nitric oxide (NO), as an intercellular signaling agent, can react rapidly with the oxyhemoproteins [7, 8]. The reaction has been widely used as an assay for NO in various tissues [8, 9]. Especially the more recent crystallographic studies on Fe-NO porphyrins by Scheidt and co-workers [10], led to the synthesis, spectroscopic and structural characterization of a plethora of metalloporphyrin-diatomic model complexes [10].

In this work, Cerium (III) tetraphenylporphyrin nitrate Ce(TPP)NO₃ was synthesized. Then, the product was characterized by UV-Vis, FT-IR, fluorescence, MALDI-TOF-MS, and ¹H NMR spectral techniques.

After that, a dichloromethane (CH₂Cl₂) solution of Ce(TPP)NO₃ bubbled NO. The comparison spectra of bubbled gas molecule's Ce(TPP)NO₃ solution suggested that it could interact with NO by molecular recognition.

II. EXPERIMENTS

A. Instrumentation

UV-Vis spectra were recorded on a Varian CARY 1E UV-Vis spectrometer. FT-IR spectra were acquired as KBr discs on a Bruker VECTOR22 FTIR spectrometer. Fluorescence spectra were acquired using an F-4500 fluorescence spectrophotometer employing a 500 W Hg-Xe high-pressure lamp. Mass spectra were recorded on Bruker BIFLEX-3 MALDI-TOF-MS spectrometer and Bruker APEX IV (7.0 T) Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS). ¹H NMR spectra were acquired using a Bruker ARX-400 NMR spectrometer, and CDCl₃ was used as a NMR solvent.

B. Reagents

Meso-tetraphenylporphyrin (TPP, >98%) was purchased from Hunan Jineng New Material Co., Ltd. (Changsha, Hunan Province, China). Dichloromethane and ethanol (A.R. analytical reagent) were purchased from Tianjin Siyou Co., Ltd. (Tianjin, China). Chloroform (A.R.), Ce(NO₃)₃·6H₂O (chemical pure), Na₂SO₄

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(A.R.) and neutral aluminum oxide (Al₂O₃) (200–300 mesh) were dried before using. The calibration gases of NO+N₂ (5000 ppmv) were purchased from Beijing Gas Center (Beijing, China).

C. Preparation of Ce(TPP)NO₃

Ce(TPP)NO₃ was synthesized by modification of the methods described in metal-porphyrin synthesis processes [11–13]. A solution 30 mg TPP and 200 mg Ce(NO₃)₃·6H₂O in mixture solution of CHCl₃ and C₂H₅OH (*V*:*V*=1:1) were refluxed in three-necked round-bottomed flask under the protection of a dry nitrogen stream for 7 h. The mixture was diluted with 25 mL of CH₂Cl₂ and washed three times with 15 mL of deionized water. The organic layer was dried (Na₂SO₄) and filtrated, and upon it, the filtrate was concentrated to about 5 mL. Chromatography on an alumina (Al₂O₃) (200–300 mesh) column (3 cm×30 cm, poured as a CH₂Cl₂ slurry) with CH₂Cl₂ elution yielded residual TPP. Elution with dichloromethane: absolute ethyl alcohol (1:1) afforded fractions that were concentrated and evaporated to dryness under reduced pressure at 433 K for 4 h.

III. RESULTS AND DISCUSSION

A. Composition of the complexes

The reaction of Ce(NO₃)₃ with TPP in CHCl₃ and absolute ethanol may be represented by the following equation:



1. UV-Vis spectra

UV-Vis spectra of Ce(TPP)NO₃ and TPP are shown in Fig.1. The absorption bands of TPP appeared at 418, 515, 550, 590, and 645 nm, which are in good agreement with the results in Ref.[14]. The absorption bands of the complex Ce(TPP)NO₃ appeared at 422, 517, 553, and 591 nm. The absorption spectra showed typical Soret bands and several Q bands. Compared with TPP, the number of complex's absorption bands decreased and the absorption bands exhibited small shifts to longer wavelengths.

The peak at 422 nm was assigned to the Soret band of Ce(TPP)NO₃ arising from the a_{1u}(π)-e_g^{*}(π) transition [15]. Similar Soret absorption bands (B bands) were observed for most porphyrinic complexes and attributed to excitonic interactions between the large soret transition dipoles of the constituent porphyrin chromophores. These Q bands of Ce(TPP)NO₃ were attributed to the

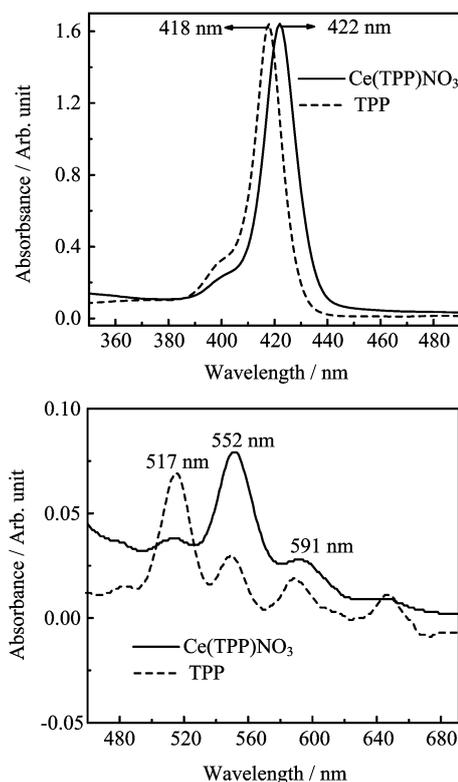


FIG. 1 UV-Vis absorption spectra of Ce(TPP)NO₃ and TPP.

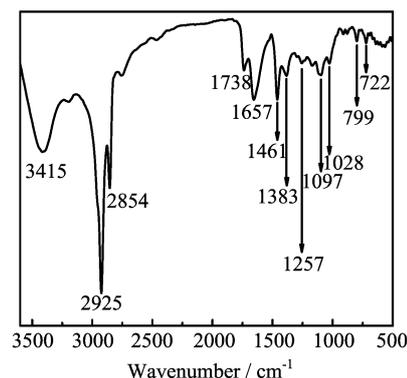


FIG. 2 FT-IR spectrum of Ce(TPP)NO₃.

a_{2u}(π)-e_g^{*}(π) transitions [15]. The UV-Vis spectral results of complex showed bands characteristic of metal-porphyrins [16].

2. FT-IR spectra

The important band frequencies and assignments of complex are presented in Fig.2. The bands at 3309 and 968 cm⁻¹ in Ce(TPP)NO₃ were due to the N–H stretching and bending vibration of the porphyrin core. The N–H stretching and bending vibration bands in the complex disappeared, since the hydrogen atoms were re-

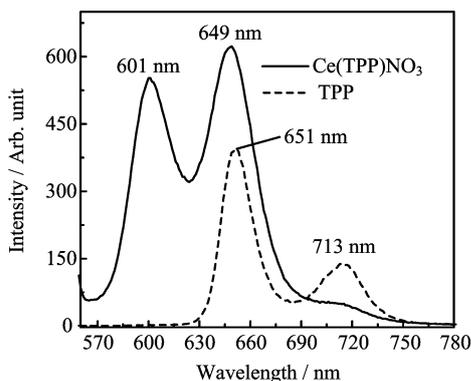


FIG. 3 Fluorescence emission ($\lambda_{\text{exc}}=550$ nm) spectra of $\text{Ce}(\text{TPP})\text{NO}_3$ and TPP.

placed by cerium ion to form a Ce–N bond [13]. The bands in 1723 cm^{-1} of the complexes, which did not exist in the free porphyrin and transition metal porphyrin complexes, were assigned to nitrate stretching vibration [17]. The appearance of nitrate stretching vibration indicated that nitrate was coordinated to the cerium ion.

3. Fluorescence spectra

Stable-state fluorescence spectra with selective excitation of the $\text{Ce}(\text{TPP})\text{NO}_3$ and TPP moieties were recorded and shown in Fig.3. Fluorescence signals were detected for metalloporphyrins under the particular experimental conditions. Upon excitation at 550 nm, where the P-part of TPP absorbs, strong fluorescence with maximum emission positions of Q^* at 651 and 713 nm were observed, while the emission peaks of $\text{Ce}(\text{TPP})\text{NO}_3$ were situated at 601 and 649 nm which were some 50 nm blue shifted compared to TPP. So the conclusion was drawn that $\text{Ce}(\text{TPP})\text{NO}_3$ could emit fluorescence.

4. Mass spectrometry spectra

MS spectrum of the original $\text{Ce}(\text{TPP})\text{NO}_3$ solution was detected using a MALDI-TOF mass spectrometer, and shown in Fig.4. From the MS spectrum, the peak at $m/z=813.9$ was due to the molecular ion peak of $\text{Ce}(\text{TPP})\text{NO}_3$. Its theoretical molecular weight of $\text{Ce}(\text{TPP})\text{NO}_3$ was 814.8. This spectrum indicated that a new lanthanide porphyrin complex, $\text{Ce}(\text{TPP})\text{NO}_3$, which has not been reported so far, was synthesized.

5. ^1H NMR spectral results

The ^1H NMR spectrum chemical shift values of $\text{Ce}(\text{TPP})\text{NO}_3$ in CDCl_2 are δ 7.258 (12H, *m*, *p*-PhH), 7.046 (8H, *m*-PhH), 7.464 (8H, *o*-PhH), 8.011 and 7.995

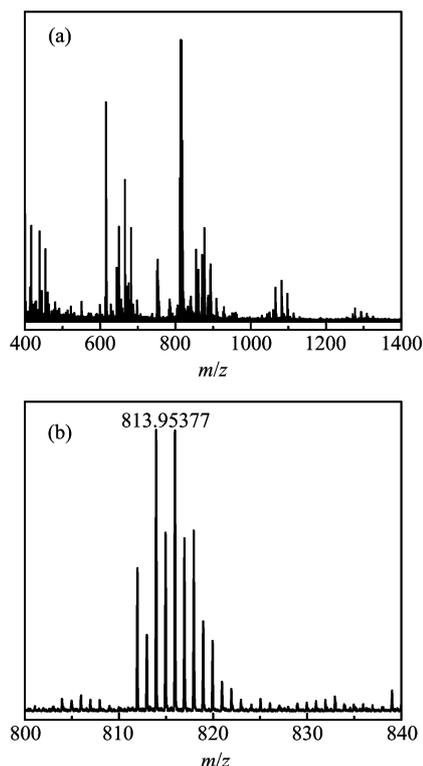


FIG. 4 MALDI-TOF MS spectra of (a) $\text{Ce}(\text{TPP})\text{NO}_3$ with (b) enlarged one.

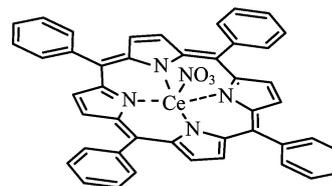


FIG. 5 Proposed structure of complex $\text{Ce}(\text{TPP})\text{NO}_3$.

(8H, *d*, β -pyrrole ring). The signal peak at -2.76 (2H, pyrrole N–H) of TPP disappeared, since the hydrogen atoms in the N–H bond were replaced by cerium atom.

From the above results, the following conclusion was drawn: one molecule of the TPP was coordinated to a cerium ion in a tetradentate fashion and one nitrate as $\text{Ce}(\text{TPP})\text{NO}_3$. With complementary density functional theory calculation, the geometry of this complex was determined [6, 18]. So the possible structure of $\text{Ce}(\text{TPP})\text{NO}_3$ was proposed, as shown in Fig.5.

B. Recognition process of NO with $\text{Ce}(\text{TPP})\text{NO}_3$

A solution of $\text{Ce}(\text{TPP})\text{NO}_3$ in CH_2Cl_2 was put in a cold trap and bubbled NO. After that, it was investigated by UV-Vis, FT-IR, and fluorescence spectral techniques.

When NO gas was bubbled through the solution, the

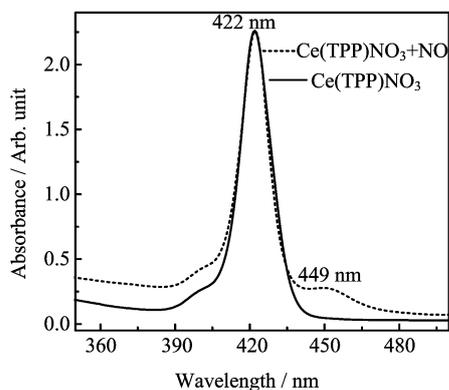


FIG. 6 UV-Vis absorption spectra of Ce(TPP)NO₃ and Ce(TPP)NO₃ solution after bubbling NO for 30 min.

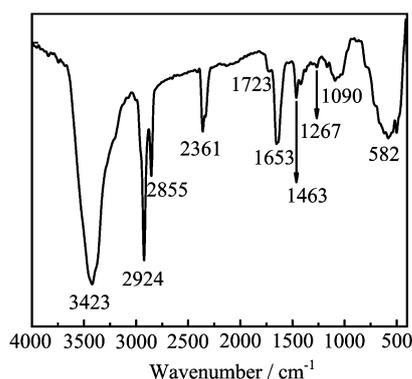


FIG. 7 FT-IR spectrum of the Ce(TPP)NO₃ solution after bubbling NO for 30 min.

color changed from red to green, so we inferred that Ce(TPP)NO₃ could interact with NO. From the UV-Vis spectra of the Ce(TPP)NO₃ and the Ce(TPP)NO₃ solution after bubbling NO for 30 min (Fig.6), we could see a new Soret band at 449 nm which suggested that Ce(TPP)NO₃ reacted with NO, resulting in the formation of a new compound.

To clarify the bonding sites of Ce(TPP)(NO)NO₃, FT-IR spectrum of the Ce(TPP)NO₃ solution after bubbling NO for 30 min was obtained to determine possible bonds by analysis of their vibrational bands (Fig.7). The frequencies of Ce–NO and N–O stretching bands appeared at 582 and 1653 cm⁻¹, respectively [19].

The fluorescence emission spectra of the Ce(TPP)NO₃ and the Ce(TPP)NO₃ solution after bubbling NO for 30 min (Fig.8) showed a decrease in the fluorescence intensity of the Ce(TPP)NO₃ solution after bubbling NO for 30 min at 600 nm. The fluorescence of Ce(TPP)NO₃ was significantly quenched, and this phenomenon could be attributed to electron transfer taking place from the P part of Ce(TPP)NO₃ to an acceptor molecule.

Since the odd electron resides in a NO π* orbital, it could involve with the metal center. Thus, in terms of

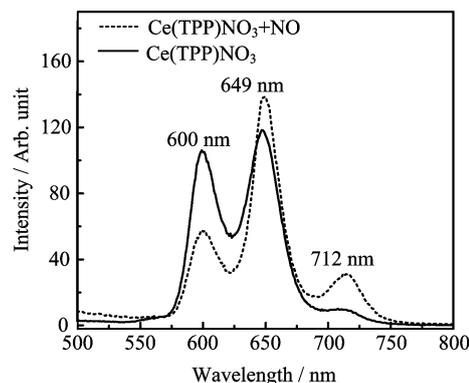


FIG. 8 Fluorescence emission ($\lambda_{\text{exc}}=550$ nm) spectra of Ce(TPP)NO₃ and the Ce(TPP)NO₃ solution after bubbling NO for 30 min.

its reactions with Fe (II) and Fe(III) hemes [20], NO acted as a normal two-electron donor ligand in the initial stages of its interaction with the metal center. So we concluded that NO interacted with cerium atom [21]. In this reaction, Ce(TPP)NO₃ reacted very rapidly to form six-coordinate Ce(TPP)(NO)(NO₃). The vibrational modes due to the metalbound axial ligands are enhanced by electronic coupling of the orbitals of the ligand to the metalloporphyrin electronic orbitals.

When the compressed N₂ was poured into the Ce(TPP)(NO)(NO₃) solution continually for 1 h, the color of Ce(TPP)(NO)(NO₃) solution changed from green to red. The spectra results indicated that this complex could be reduced to Ce(TPP)NO₃.

IV. CONCLUSION

In present work, a novel complex (Ce(TPP)NO₃) was synthesized using TPP and Ce(NO₃)·6H₂O in the mixtures solution of CHCl₃ and C₂H₅OH (V:V=1:1). Then, the synthesized product was characterized by various spectral technologies. The novel complex Ce(TPP)NO₃ in CH₂Cl₂ solution bubbled NO, and the spectral results suggested that Ce(TPP)NO₃ could interact with NO, which provided the basis for molecular recognition.

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- [1] J. P. Collman, P. S. Wagenknecht, and J. E. Hutchinson, *Angew. Chem. Int. Ed.* **33**, 1537 (1994).
- [2] Y. Y. Qian, K. L. Wong, M. W. Zhang, T. Y. Kwok, T. C. Tat, and K. S. Chan, *Tetrahedron Lett.* **53**, 1571 (2012).
- [3] A. V. Leonitiev and D. M. Rudkevich, *J. Am. Chem. Soc.* **127**, 14126 (2005).
- [4] L. Guo and B. Yan, *Inorg. Chem. Commun.* **14**, 1833 (2011).
- [5] C. P. Wong, R. F. Venteicher, and W. Horrocks, *J. Am. Chem. Soc.* **96**, 7149 (1974).
- [6] J. W. Buchler and T. Dippell, *Eur. J. Inorg. Chem.* 445 (1998).
- [7] N. P. Doyle and J. W. Hoekstra, *J. Inorg. Biochem.* **14**, 351 (1981).
- [8] E. Nowack, D. Kubitzek, and G. Kojda, *NeuroProctols* **1**, 133 (1992).
- [9] S. Archer, *FASEB J.* **7**, 349 (1993).
- [10] G. R. A. Wyllie and W. R. Scheidt, *Chem. Rev.* **102**, 1067 (2002).
- [11] Z. X. Zhao, T. F. Xie, D. M. Li, D. J. Wang, and G. F. Liu, *Synth. Met.* **123**, 33 (2001).
- [12] H. S. He, W. K. Wong, J. P. Guo, K. F. Li, W. Y. Wong, and W. K. Lo, *Inorg. Chim. Acta* **357**, 4379 (2004).
- [13] Z. X. Zhao, Q. H. Xu, D. M. Li, G. F. Liu, L. S. Li, and R. R. Xu, *Solid State Sci.* **3**, 339 (2001).
- [14] W. D. Jr. Horrocks and C. P. Wong, *J. Am. Chem. Soc.* **98**, 7157 (1976).
- [15] W. Q. Zhang, N. Shan, L. X. Yu, and X. Q. Wang, *Dyes Pigments* **77**, 153 (2008).
- [16] C. P. Wong and W. D. Jr. Horrocks, *Tetrahedron Lett.* 2637 (1975).
- [17] A. B. Lever, P. E. Mantovani, and B. S. Ramaswa, *Can. J. Chem.* **49**, 1957 (1971).
- [18] A. Weber-Bargioni, J. Reichert, A. P. Seitsonen, W. Auwarter, A. Schiffrin, and J. V. Barth, *J. Phys. Chem. C* **112**, 3453 (2008).
- [19] L. E. Laverman, M. Hoshino, and P. C. Ford, *J. Am. Chem. Soc.* **119**, 12663 (1997).
- [20] T. K. Das, E. K. Wilson, F. Cutruzzola, M. Brunori, and D. L. Rousseau, *Biochemistry* **40**, 10774 (2001).
- [21] G. A. Tondreau and D. A. Sweigart, *Inorg. Chem.* **23**, 1060 (1984).